



US011312817B2

(12) **United States Patent**
Storey et al.

(10) **Patent No.:** **US 11,312,817 B2**

(45) **Date of Patent:** ***Apr. 26, 2022**

(54) **POLYURETHANE POLYMERS CURED VIA AZIDO-ALKYNE CYCLOADDITION AT AMBIENT OR MILD CURING CONDITIONS**

(71) Applicants: **Covestro LLC**, Pittsburgh, PA (US);
The University Of Southern Mississippi, Hattiesburg, MS (US)

(72) Inventors: **Robson F. Storey**, Hattiesburg, MS (US); **Alan Ekin**, Coraopolis, PA (US); **R. Hunter Cooke, III**, Atlanta, GA (US); **Jie Wu**, Hattiesburg, MS (US)

(73) Assignees: **Covestro LLC**, Pittsburgh, PA (US);
The University Of Southern Mississippi, Hattiesburg, MS (US)

(*) Notice: Subject to any disclaimer, the term of this patent is extended or adjusted under 35 U.S.C. 154(b) by 112 days.

This patent is subject to a terminal disclaimer.

(21) Appl. No.: **16/693,837**

(22) Filed: **Nov. 25, 2019**

(65) **Prior Publication Data**

US 2021/0155748 A1 May 27, 2021

(51) **Int. Cl.**
C08G 18/81 (2006.01)
C08G 18/67 (2006.01)
(Continued)

(52) **U.S. Cl.**
CPC **C08G 18/8191** (2013.01); **C08G 18/12** (2013.01); **C08G 18/222** (2013.01);
(Continued)

(58) **Field of Classification Search**
CPC C08G 18/8191; C08G 18/679
See application file for complete search history.

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Primary Examiner — Michael L Leonard

(74) *Attorney, Agent, or Firm* — Richard P. Bender; John E. Mrozinski, Jr.

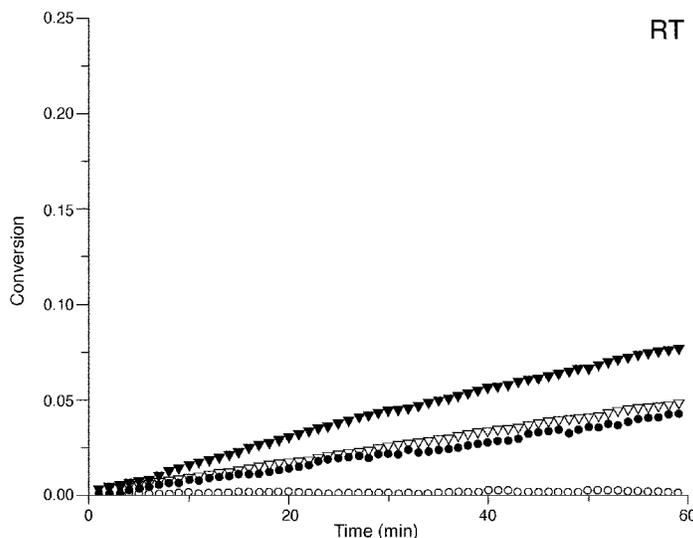
(57) **ABSTRACT**

An alternative polyurethane composition is provided which comprises a reaction product of an azidated polyol and a poly(alkynyl carbamate) prepolymer reacted at a temperature of from 20° C. to 120° C., wherein the poly(alkynyl carbamate) prepolymer comprises a reaction product of a polyisocyanate and a stoichiometric equivalent of an alkynol of the formula (I),



and wherein R¹ is an electron-withdrawing group selected from the group consisting of carbonyl, ester, amide, and urethane and R² is a linear or branched alkyl chain having from 1 to 15 carbon atoms. The inventive alternative polyurethane composition position may be used to provide adhesives, sealants, films, elastomers, castings, foams, and composites.

24 Claims, 4 Drawing Sheets



- (51) **Int. Cl.**
C08G 18/22 (2006.01)
C08G 18/38 (2006.01)
C08G 18/78 (2006.01)
C08G 18/12 (2006.01)
- (52) **U.S. Cl.**
 CPC *C08G 18/3836* (2013.01); *C08G 18/679*
 (2013.01); *C08G 18/7831* (2013.01); *C08G*
18/7837 (2013.01); *C08G 18/7887* (2013.01)

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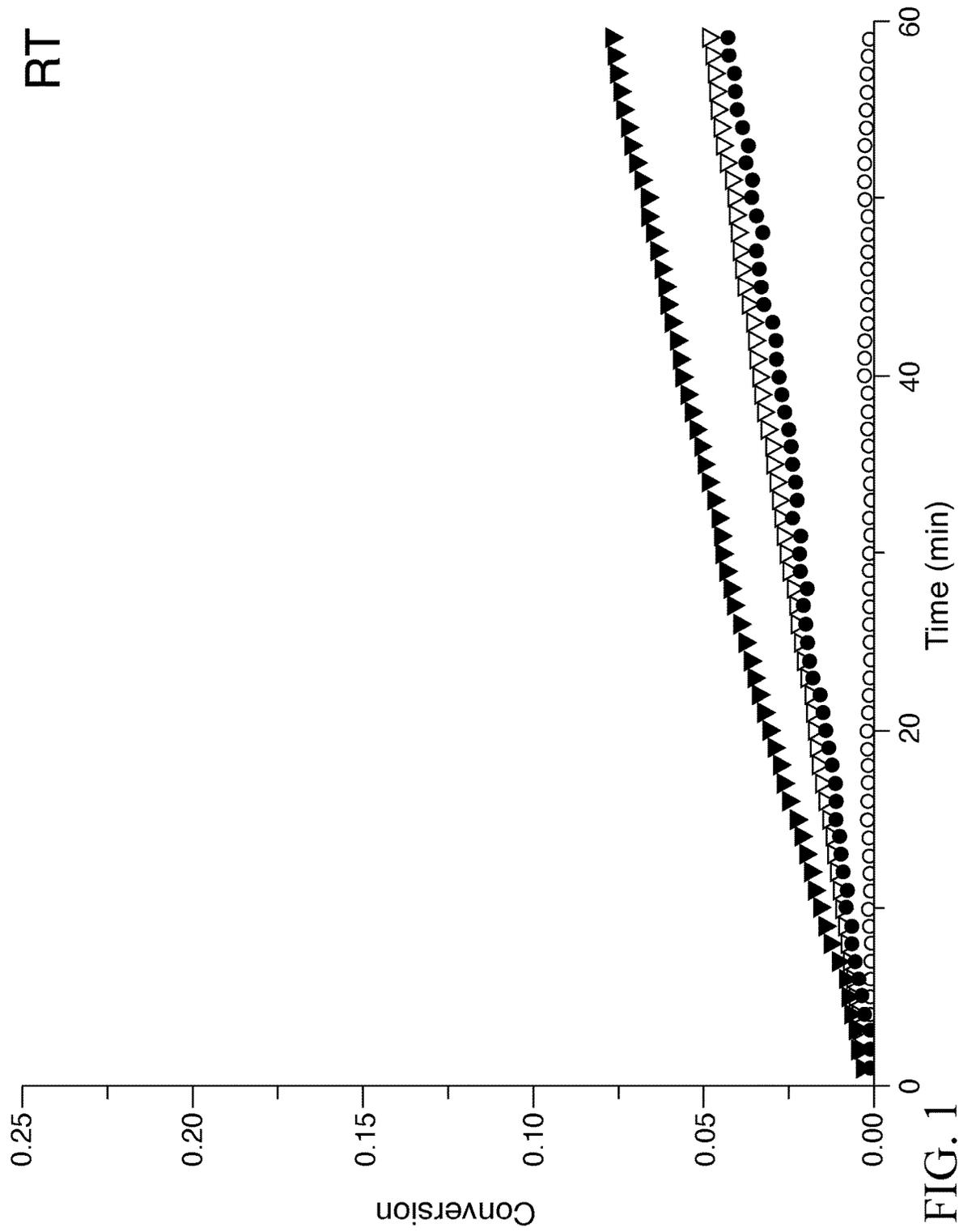
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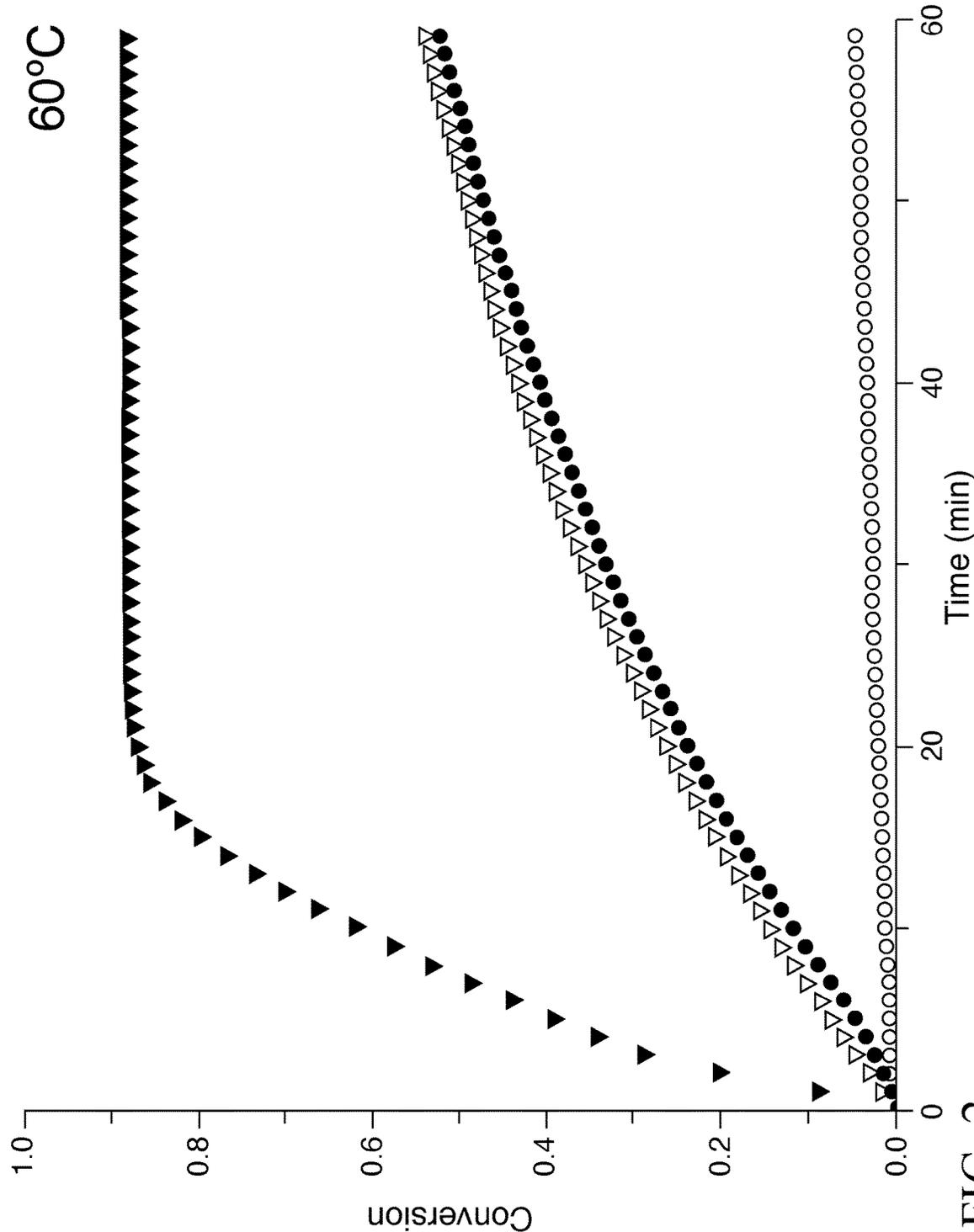


FIG. 2

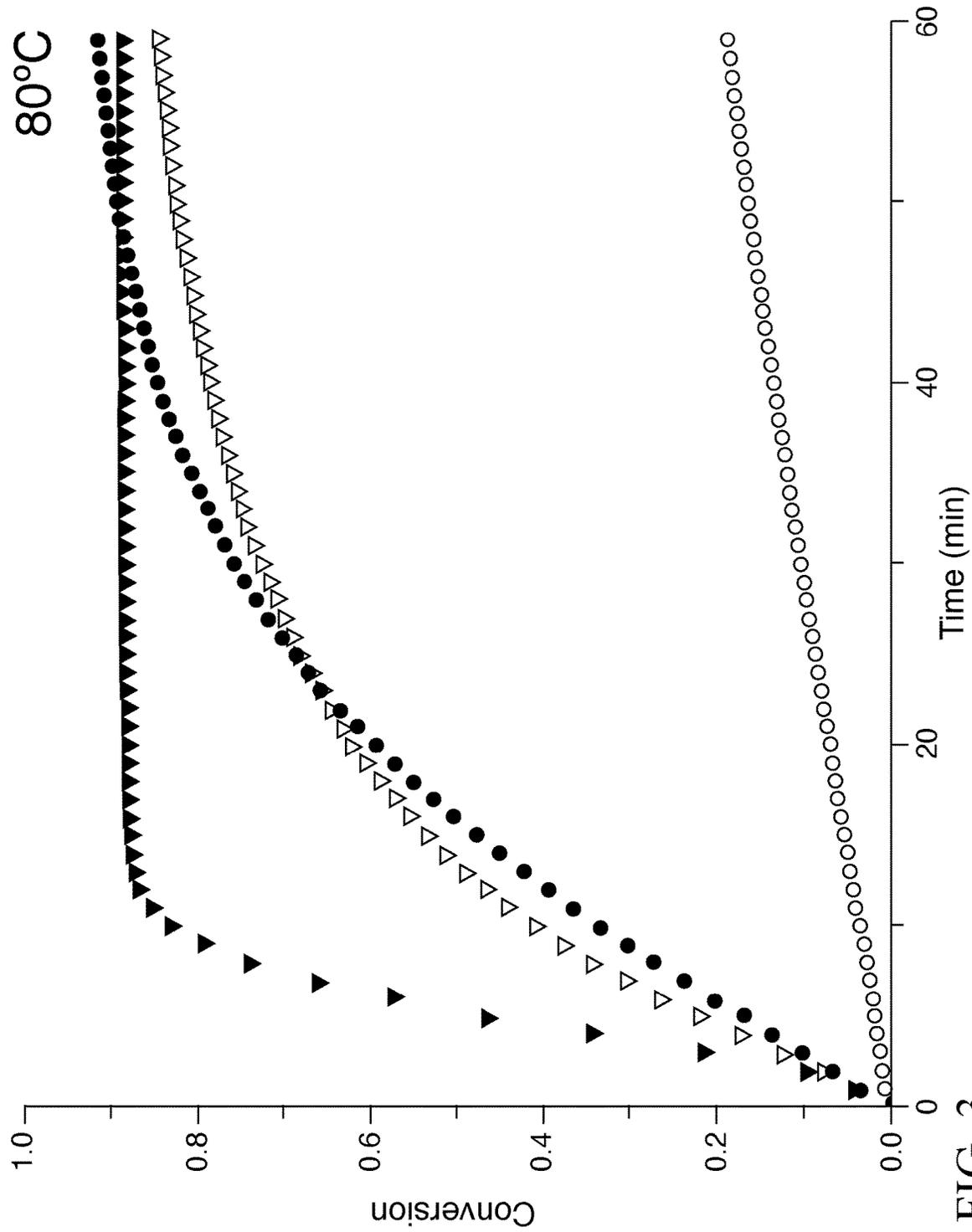


FIG. 3

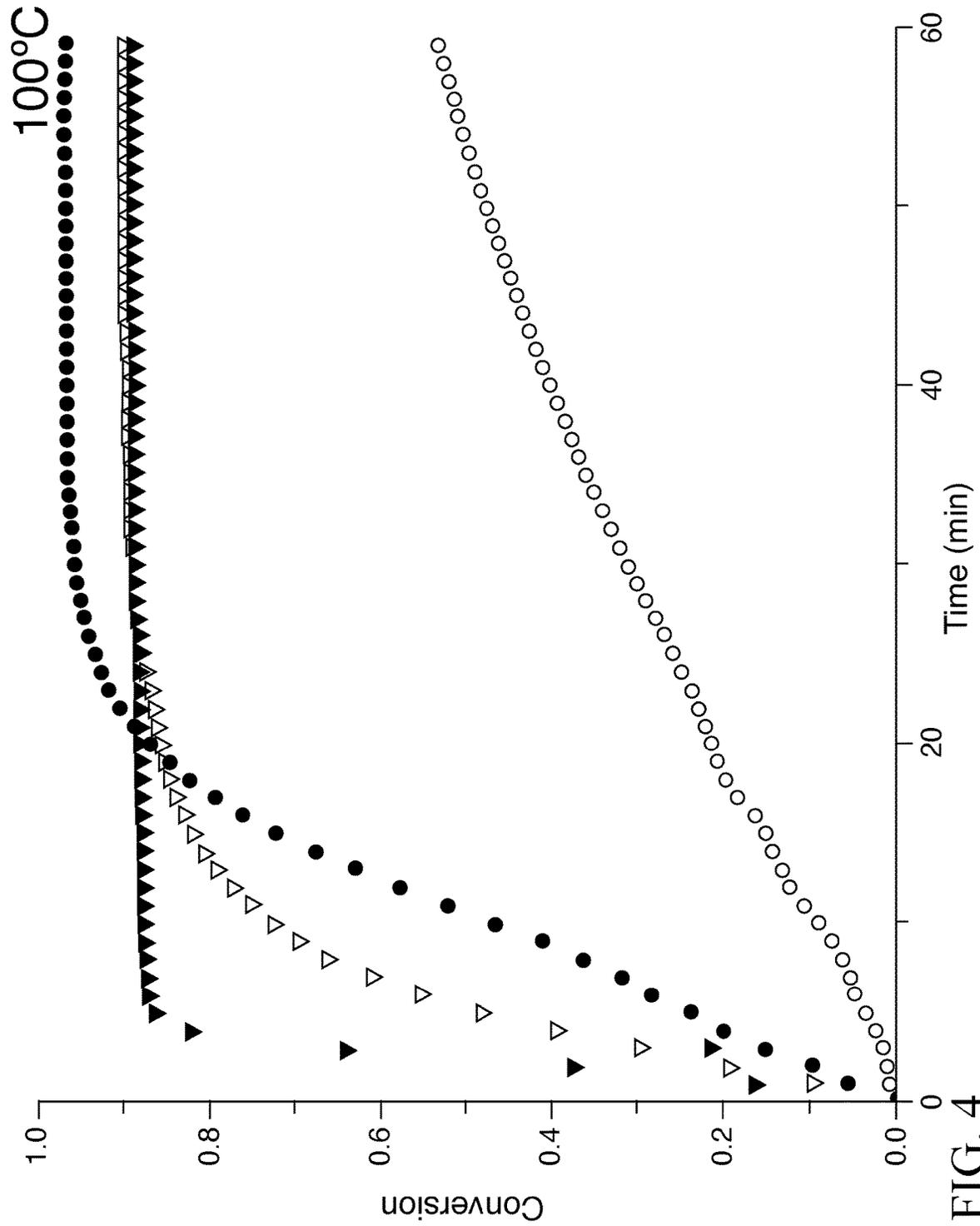


FIG. 4

**POLYURETHANE POLYMERS CURED VIA
AZIDO-ALKYNE CYCLOADDITION AT
AMBIENT OR MILD CURING CONDITIONS**

FIELD OF THE INVENTION

The present invention relates to alternative polyurethane compositions which are reaction products of a poly(alkynyl carbamate) prepolymer and an azidated polyol. The azide and alkyne groups react in a 1,3-dipolar cycloaddition to form 1,4- and 1,5-disubstituted triazoles. At least one of the poly(alkynyl carbamate) prepolymer and the azidated polyol contain $-\text{O}(\text{C}=\text{O})-\text{NR}-$ functional groups, wherein $\text{R}=\text{hydrogen}$ or alkyl. The poly(alkynyl carbamate) prepolymer comprises the reaction product of a polyisocyanate and a stoichiometric equivalent of an alkynol of the formula (I)



wherein R^1 is an electron-withdrawing group selected from the group consisting of carbonyl, ester, amide, and urethane and R^2 is a linear or branched alkyl chain having from 1 to 15 carbon atoms. The alternative polyurethane compositions may be thermally cured or may be cured with Cu^I -containing catalysts and are suitable for use as coatings, adhesives, sealants, films, elastomers, castings, foams, and composites.

BACKGROUND OF THE INVENTION

“Click chemistry” is a term first used by Sharpless et al. (*Angew. Chem. Int. Ed.* 2001, 40, 2004-2021) to describe a family of synthetic reactions, which attempt to imitate nature by joining small molecules together with heteroatom links. Sharpless et al. stated a number of criteria that a reaction must meet to be considered a “click” type reaction. These criteria include the reaction (a) must be modular; (b) must have a wide scope; (c) must provide high yields; (d) must produce inoffensive by-products (which can be removed by non-chromatographic methods); (e) must be stereospecific; and (f) must involve simple reaction conditions (insensitive to water and oxygen) and product isolation. Finally, the reaction should use readily available starting materials, reactants, and solvents which are easily removed.

One example of a click reaction which has attracted wide attention is the copper catalyzed azide-alkyne cycloaddition (CuAAC). This azide-alkyne cycloaddition was first described by Huisgen in 1963 and was carried out in the absence of a catalyst, requiring elevated temperatures and giving a mixture of products (namely the 1,4 and 1,5-substituted triazoles). The Cu^I -catalyzed cycloaddition was discovered independently by Meldal (*Macromol. Rapid. Comm.* 2008, 29 (12-13), 1016-1051) and Sharpless et al. The benefit seen with these copper-catalyzed reactions was that they could be performed at room temperature and resulted in the exclusive formation of 1,4-substituted triazole products. Another advantage of this cycloaddition is that the azide and alkyne moieties are generally unreactive towards a wide range of functional groups, which eliminates the need for extensive use of protecting groups. This advantage is a key to the reaction’s popularity in a number of scientific fields such as the biomedical field and material science.

Although the initial investigations of 1,3-dipolar cycloadditions via click chemistry focused on the functionalization and attachment of small molecules to biochemical molecules, U.S. Pat. No. 8,101,238 issued to Fokin et al. describes adhesive polymers which are formed from polyvalent alkynes and azides and can be assembled into cross-

linked polymer networks by copper catalysis. The Fokin et al. patent describes the formation of coatings on copper metal surfaces which act as a catalyst for the alkynes and azides to form linear polymers including up to 22 units of a diazide and dialkyne or cross-linked polymeric networks. The compositions disclosed in Fokin et al. were proposed for use in applications such as adhesives and coatings and for combination with cement and other materials.

Polymeric triazoles constructed by 1,3-dipolar cycloaddition are also described in U.S. Pat. No. 7,772,358 issued to Tang et al. The compounds of Tang et al. are prepared by thermal conversion at about 100°C . without the addition of a catalyst, which resulted in the formation of both 1,4- and 1,5-disubstituted triazoles. These compositions are described by Tang et al. as being “hyper-branched”, which is a result of the exclusive use of tri- or higher substituted alkynes and azides during preparation. The advantage of these compositions is that their preparation does not involve the use of additional solvents or catalysts, which might have detrimental effects on the resulting properties. This benefit, however, is somewhat negated by the need to cure the compositions at elevated temperatures.

Liu, X.-M. et al. in *Biomacromolecules* 2007, 8, 2653-2658 describe the synthesis of linear poly(ethylene glycol)s using 1,3-dipolar cycloaddition for chain extension. Liu et al. disclose that poly(ethylene glycol)s having pendant alkyne moieties are reacted with 2,2-bis(azidomethyl)propane-1,3-diol and copper sulfate/sodium ascorbate.

A significant disadvantage of the above-described reactions is the required use of di- and polyazides, which have relatively high nitrogen contents. For example, Fokin et al. in U.S. Pat. No. 8,101,238 describe compounds having nitrogen contents of up to about 60% in the form of azides. Such compounds are impracticable for industrial application due to the compounds’ explosiveness. The compounds of Tang et al. and Xin-Ming et al. have nitrogen contents in the form of azides of about 23% and 43%, respectively, which pose problems when the azide compounds are handled as such.

Ossipov et al. (*Macromolecules* 2006, 39, 1709-1718) describe the preparation of poly(vinyl alcohol)-based hydrogels via 1,3-dipolar cycloaddition, in which a first poly(vinylalcohol) is functionalized with azide functionalities and a second poly(vinyl alcohol) is functionalized with alkyne functionalities, and subsequently the two poly(vinylalcohol)s are reacted with each other by cyclization of the alkyne and azide groups. Ossipov et al. also disclose that azide terminated poly(ethylene glycol)s may be used as a replacement for the azide-modified poly(vinylalcohol).

Carter et al. in U.S. Pat. No. 9,790,398 disclose the synthesis of both a diazide monomer and a dialkyne monomer from 4,4'-diphenylmethane diisocyanate (MDI). The inventors also created a diazide monomer by reaction of sodium azide with diglycidyl ether of poly(propylene oxide). Carter et al. disclose the synthesis of only one polymer produced by CuAAC catalyzed reaction of azide-functional poly(propylene glycol) diglycidyl ether with the dialkyne of MDI.

U.S. Pat. Pub. No. 2016/0311973 in the name of Yang et al. is directed to waterborne dispersion coatings that cure by a 1,3-dipolar cycloaddition. Yang et al. disclose hexamethylene diisocyanate (HDI)-based polyurethane/urea dispersions possessing pendent propargyl groups, HDI-based polyurethane/urea dispersions possessing pendent azide groups, and also alkyd and acrylic type waterborne polymers possessing either alkyne or azide pendent groups.

Both the Carter et al. and Yang et al. references start from small molecules and polymerize these materials to give the final alternative polyurethane products.

Despite the above-described advancements in technology, the 1,3-dipolar cycloaddition of multivalent azides and alkynes has not been described in combination with pre-polymer precursors to which the azide and alkyne groups have been attached. Such prepolymers would have the advantage that the azide content of a prepolymer relative to its total weight could be low enough to minimize the risk of explosions, while the number of azides in the prepolymer molecules can be higher than two allowing the formation of cross-linked systems.

To reduce or eliminate problem(s), therefore, a need continues to exist in the art for ways of producing alternative polyurethane compositions which rely on simple modification of existing prepolymers.

SUMMARY OF THE INVENTION

Accordingly, the present invention reduces or eliminates problems inherent in the art by providing novel chemical intermediates and methods of preparation, and polyurethane-based coatings, adhesives, sealants, films, elastomers, castings, foams, and composites made therefrom, that cure without the presence of free isocyanates in the final curing step. Curing of the inventive coatings, adhesives, sealants, films, elastomers, castings, foams, and composites, collectively the inventive alternative polyurethane compositions, involves reaction of an alkyne-functional resin with an azide-functional resin (i.e. Huisgen azido-alkyne cycloaddition) and may be carried out at ambient or mild temperatures or may be cured with Cu^I-containing catalysts. The inventive alternative polyurethane compositions may be used in the production of coatings, adhesives, sealants, films, elastomers, castings, foams, and composites.

These and other advantages and benefits of the present invention will be apparent from the Detailed Description of the Invention herein below.

BRIEF DESCRIPTION OF THE FIGURES

The present invention will now be described for purposes of illustration and not limitation in conjunction with the figures, wherein:

FIG. 1 depicts the isothermal curing kinetics of the inventive composition at room temperature;

FIG. 2 depicts the isothermal curing kinetics of the inventive composition at a temperature of 60° C.;

FIG. 3 depicts the isothermal curing kinetics of the inventive composition at a temperature of 80° C.; and

FIG. 4 depicts the isothermal curing kinetics of the inventive composition at a temperature of 100° C.

DETAILED DESCRIPTION OF THE INVENTION

The present invention will now be described for purposes of illustration and not limitation. Except in the operating examples, or where otherwise indicated, all numbers expressing quantities, percentages, and so forth in the specification are to be understood as being modified in all instances by the term "about."

Any numerical range recited in this specification is intended to include all sub-ranges of the same numerical precision subsumed within the recited range. For example, a range of "1.0 to 10.0" is intended to include all sub-ranges

between (and including) the recited minimum value of 1.0 and the recited maximum value of 10.0, that is, having a minimum value equal to or greater than 1.0 and a maximum value equal to or less than 10.0, such as, for example, 2.4 to 7.6. Any maximum numerical limitation recited in this specification is intended to include all lower numerical limitations subsumed therein and any minimum numerical limitation recited in this specification is intended to include all higher numerical limitations subsumed therein. Accordingly, Applicant reserves the right to amend this specification, including the claims, to expressly recite any sub-range subsumed within the ranges expressly recited herein. All such ranges are intended to be inherently described in this specification such that amending to expressly recite any such sub-ranges would comply with the requirements of 35 U.S.C. § 112(a), and 35 U.S.C. § 132(a). The various embodiments disclosed and described in this specification can comprise, consist of, or consist essentially of the features and characteristics as variously described herein.

Any patent, publication, or other disclosure material identified herein is incorporated by reference into this specification in its entirety unless otherwise indicated, but only to the extent that the incorporated material does not conflict with existing definitions, statements, or other disclosure material expressly set forth in this specification. As such, and to the extent necessary, the express disclosure as set forth in this specification supersedes any conflicting material incorporated by reference herein. Any material, or portion thereof, that is said to be incorporated by reference into this specification, but which conflicts with existing definitions, statements, or other disclosure material set forth herein, is only incorporated to the extent that no conflict arises between that incorporated material and the existing disclosure material. Applicant reserves the right to amend this specification to expressly recite any subject matter, or portion thereof, incorporated by reference herein.

Reference throughout this specification to "various non-limiting embodiments," "certain embodiments," or the like, means that a particular feature or characteristic may be included in an embodiment. Thus, use of the phrase "in various non-limiting embodiments," "in certain embodiments," or the like, in this specification does not necessarily refer to a common embodiment, and may refer to different embodiments. Further, the particular features or characteristics may be combined in any suitable manner in one or more embodiments. Thus, the particular features or characteristics illustrated or described in connection with various or certain embodiments may be combined, in whole or in part, with the features or characteristics of one or more other embodiments without limitation. Such modifications and variations are intended to be included within the scope of the present specification.

The grammatical articles "a", "an", and "the", as used herein, are intended to include "at least one" or "one or more", unless otherwise indicated, even if "at least one" or "one or more" is expressly used in certain instances. Thus, these articles are used in this specification to refer to one or more than one (i.e., to "at least one") of the grammatical objects of the article. By way of example, and without limitation, "a component" means one or more components, and thus, possibly, more than one component is contemplated and may be employed or used in an implementation of the described embodiments. Further, the use of a singular noun includes the plural, and the use of a plural noun includes the singular, unless the context of the usage requires otherwise.

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In a first aspect, the present invention is directed to an alternative polyurethane composition comprising: a reaction product of an azidated polyol and a poly(alkynyl carbamate) prepolymer reacted at a temperature of from 20° C. to 120° C., wherein the poly(alkynyl carbamate) prepolymer comprises a reaction product of a polyisocyanate and a stoichiometric equivalent of an alkynol of the formula (I),



and wherein R¹ is an electron-withdrawing group selected from the group consisting of carbonyl, ester, amide, and urethane and R² is a linear or branched alkyl chain having from 1 to 15 carbon atoms. The reaction of the azidated polyol and poly(alkynyl carbamate) prepolymer may optionally occur in the presence of a Cu^I-containing catalyst.

In a second aspect, the present invention is directed to a process of producing an alternative polyurethane composition, the process comprising: reacting a polyisocyanate with a stoichiometric equivalent of an alkynol of the formula (I),



to produce a poly(alkynyl carbamate) prepolymer, and reacting the poly(alkynyl carbamate) prepolymer with an azidated polyol at a temperature of from 20° C. to 120° C. to produce the alternative polyurethane composition, wherein R¹ is an electron-withdrawing group selected from the group consisting of carbonyl, ester, amide, and urethane and R² is a linear or branched alkyl chain having from 1 to 15 carbon atoms. The reaction of the azidated polyol and poly(alkynyl carbamate) prepolymer may optionally occur in the presence of a Cu^I-containing catalyst.

In a third aspect, the present invention is directed to coatings, adhesives, sealants, films, elastomers, castings, foams, and composites comprising the inventive alternative polyurethane composition according to the previous two paragraphs.

As used herein, the term “polymer” encompasses prepolymers, oligomers, and both homopolymers and copolymers; the prefix “poly” in this context refers to two or more. As used herein, the term “molecular weight”, when used in reference to a polymer, refers to the number average molecular weight, unless otherwise specified.

As used herein, the term “polyol” refers to compounds comprising at least two free hydroxy groups. Polyols include polymers comprising pendant and terminal hydroxy groups.

As used herein, the term “coating composition” refers to a mixture of chemical components that will cure and form a coating when applied to a substrate.

The terms “adhesive” or “adhesive composition”, refers to any substance that can adhere or bond two items together. Implicit in the definition of an “adhesive composition” or “adhesive formulation” is the concept that the composition or formulation is a combination or mixture of more than one species, component or compound, which can include adhesive monomers, oligomers, and polymers along with other materials.

A “sealant” or “sealant composition” refers to a composition which may be applied to one or more surfaces to form a protective barrier, for example to prevent ingress or egress of solid, liquid or gaseous material or alternatively to allow selective permeability through the barrier to gas and liquid. In particular, it may provide a seal between surfaces.

A “film composition” refers to a mixture of chemical components that will cure and form a thin flexible strip of material, i.e., a “film”.

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An “elastomer” refers to a polymeric composition that has high elongation and flexibility or elasticity. Elastomers may be made from natural rubber, polyurethanes, polybutadiene, neoprene, and silicone.

A “casting” or “casting composition” refers to a mixture of liquid chemical components which is usually poured into a mold containing a hollow cavity of the desired shape, and then allowed to solidify.

A “foam” is produced by mixing a polyol and an isocyanate along with an amine or organometallic catalyst and a combination of water and a hydrofluorocarbon blowing agent.

A “composite” or “composite composition” refers to a material made from one or more polymers, containing at least one other type of material (e.g., a fiber) which retains its identity while contributing desirable properties to the composite. A composite has different properties from those of the individual polymers/materials which make it up.

The terms “cured,” “cured composition” or “cured compound” refers to components and mixtures obtained from reactive curable original compound(s) or mixture(s) thereof which have undergone chemical and/or physical changes such that the original compound(s) or mixture(s) is(are) transformed into a solid, substantially non-flowing material. A typical curing process may involve crosslinking.

The term “curable” means that an original compound(s) or composition material(s) can be transformed into a solid, substantially non-flowing material by means of chemical reaction, crosslinking, radiation crosslinking, or the like. Thus, compositions of the invention are curable, but unless otherwise specified, the original compound(s) or composition material(s) is(are) not cured.

The components useful in the present invention comprise a polyisocyanate. As used herein, the term “polyisocyanate” refers to compounds comprising at least two unreacted isocyanate groups, such as three or more unreacted isocyanate groups. The polyisocyanate may comprise diisocyanates such as linear aliphatic polyisocyanates, aromatic polyisocyanates, cycloaliphatic polyisocyanates and aralkyl polyisocyanates.

Suitable polyisocyanates for use in embodiments of the invention include, organic diisocyanates represented by the formula



wherein R represents an organic group obtained by removing the isocyanate groups from an organic diisocyanate having (cyclo)aliphatically bound isocyanate groups and a molecular weight of 112 to 1000, preferably 140 to 400.

Preferred diisocyanates for the invention are those represented by the formula wherein R represents a divalent aliphatic hydrocarbon group having from 4 to 18 carbon atoms, a divalent cycloaliphatic hydrocarbon group having from 5 to 15 carbon atoms, or a divalent araliphatic hydrocarbon group having from 7 to 15 carbon atoms.

Examples of the organic diisocyanates which are particularly suitable for the present invention include 1,4-tetramethylene diisocyanate, 1,6-hexamethylene diisocyanate, 2,2,4-trimethyl-1,6-hexamethylene diisocyanate, 1,12-dodecamethylene diisocyanate, cyclohexane-1,3- and 1,4-diisocyanate, 1-isocyanato-2-isocyanato-methyl cyclopentane, 1-isocyanato-3-isocyanatomethyl-3,5,5-trimethyl cyclohexane (isophorone diisocyanate or IPDI), bis-(4-isocyanatocyclohexyl)methane, 1,3- and 1,4-bis(isocyanatomethyl)-cyclohexane, bis-(4-isocyanato-3-methyl-cyclohexyl)-methane, $\alpha,\alpha,\alpha',\alpha'$ -tetramethyl-1,3- and 1,4-xylene diisocyanate, 1-isocyanato-1-methyl-4(3)-

isocyanato-methyl cyclohexane, and 2,4- and 2,6-hexahydrotoluene diisocyanate, toluene diisocyanate (TDI), diphenylmethane diisocyanate (MDI), pentane diisocyanate (PDI)—bio-based), and, isomers of any of these; or combinations of any of these. Mixtures of diisocyanates may also be used. Preferred diisocyanates include 1,6-hexamethylene diisocyanate, isophorone diisocyanate, and bis(4-isocyanatocyclohexyl)-methane because they are readily available and yield relatively low viscosity oligomers.

Polyisocyanate adducts containing isocyanurate, iminoxadiazine dione, urethane, biuret, allophanate, uretdione and/or carbodiimide groups are also suitable for use in the present invention, and may be prepared from the same organic groups, R, described above. Such polyisocyanates may have isocyanate functionalities of 3 or more and can be prepared, for example, by the trimerization or oligomerization of diisocyanates or by the reaction of diisocyanates with polyfunctional compounds containing hydroxyl or amine groups. In certain embodiments, the polyisocyanate is the isocyanurate of hexamethylene diisocyanate, which may be prepared in accordance with U.S. Pat. No. 4,324,879 at col. 3, line 5 to col. 6, line 47.

The polyols useful in the present invention may be either low molecular weight (62-399 Da, as determined by gel permeation chromatography) or high molecular weight (400 to 10,000 Da, as determined by gel permeation chromatography) materials and in various embodiments will have average hydroxyl values as determined by ASTM E222-17, Method B, of between 1000 and 10, and preferably between 500 and 50.

The polyols in the present invention include low molecular weight diols, triols and higher alcohols and polymeric polyols such as polyester polyols, polyether polyols, polycarbonate polyols, polyurethane polyols and hydroxy-containing (meth)acrylic polymers.

The low molecular weight diols, triols, and higher alcohols useful in the present invention are known to those skilled in the art. In many embodiments, they are monomeric and have hydroxyl values of 200 and above, usually within the range of 1500 to 200. Such materials include aliphatic polyols, particularly alkylene polyols containing from 2 to 18 carbon atoms. Examples include ethylene glycol, 1,4-butanediol, 1,6-hexanediol, and cycloaliphatic polyols such as cyclohexane dimethanol. Examples of triols and higher alcohols include trimethylol propane and pentaerythritol. Also useful are polyols containing ether linkages such as diethylene glycol and triethylene glycol.

In various embodiments, the suitable polyols are polymeric polyols having hydroxyl values less than 200, such as 10 to 180. Examples of polymeric polyols include polyalkylene ether polyols, polyester polyols including hydroxyl-containing polycaprolactones, hydroxy-containing (meth)acrylic polymers, polycarbonate polyols and polyurethane polymers.

Examples of polyether polyols include poly(oxytetramethylene) glycols, poly(oxyethylene) glycols, and the reaction product of ethylene glycol with a mixture of propylene oxide and ethylene oxide.

Also useful are polyether polyols formed from the oxyalkylation of various polyols, for example, glycols such as ethylene glycol, 1,4-butane glycol, 1,6-hexanediol, and the like, or higher polyols, such as trimethylol propane, pentaerythritol and the like. One commonly utilized oxyalkylation method is reaction of a polyol with an alkylene oxide, for example, ethylene oxide in the presence of an acidic or basic catalyst.

Polyester polyols can also be used as a polymeric polyol component in the certain embodiments of the invention. The polyester polyols can be prepared by the polyesterification of organic polycarboxylic acids or anhydrides thereof with organic polyols. Preferably, the polycarboxylic acids and polyols are aliphatic or aromatic dibasic acids and diols.

The diols which may be employed in making the polyester include alkylene glycols, such as ethylene glycol and butylene glycol, neopentyl glycol and other glycols such as cyclohexane dimethanol, caprolactone diol (for example, the reaction product of caprolactone and ethylene glycol), polyether glycols, for example, poly(oxytetramethylene) glycol and the like. However, other diols of various types and, as indicated, polyols of higher functionality may also be utilized in various embodiments of the invention. Such higher polyols can include, for example, trimethylol propane, trimethylol ethane, pentaerythritol, and the like, as well as higher molecular weight polyols such as those produced by oxyalkylating low molecular weight polyols. An example of such high molecular weight polyol is the reaction product of 20 moles of ethylene oxide per mole of trimethylol propane.

The acid component of the polyester consists primarily of monomeric carboxylic acids or anhydrides having 2 to 18 carbon atoms per molecule. Among the acids which are useful are phthalic acid, isophthalic acid, terephthalic acid, tetrahydrophthalic acid, hexahydrophthalic acid, adipic acid, azelaic acid, sebacic acid, maleic acid, glutaric acid, chlorogenic acid, tetrachlorophthalic acid and other dicarboxylic acids of varying types. Also, there may be employed higher polycarboxylic acids such as trimellitic acid and tricarballylic acid (where acids are referred to above, it is understood that the anhydrides of those acids which form anhydrides can be used in place of the acid). Also, lower alkyl esters of acids such as dimethyl glutamate can be used.

In addition to polyester polyols formed from polybasic acids and polyols, polycaprolactone-type polyesters can also be employed. These products are formed from the reaction of a cyclic lactone such as ϵ -caprolactone with a polyol with primary hydroxyls such as those mentioned above. Such products are described in U.S. Pat. No. 3,169,949.

In addition to the polyether and polyester polyols, hydroxy-containing (meth)acrylic polymers or (meth)acrylic polyols can be used as the polyol component.

Among the (meth)acrylic polymers are polymers of 2 to 20 percent by weight primary hydroxy-containing vinyl monomers such as hydroxyalkyl acrylate and methacrylate having 2 to 6 carbon atoms in the alkyl group and 80 to 98 percent by weight of other ethylenically unsaturated copolymerizable materials such as alkyl(meth)acrylates; the percentages by weight being based on the total weight of the monomeric charge.

Examples of suitable hydroxy alkyl(meth)acrylates are hydroxy ethyl and hydroxy butyl(meth)acrylate. Examples of suitable alkyl acrylates and (meth)acrylates are lauryl methacrylate, 2-ethylhexyl methacrylate and n-butyl acrylate.

In addition to the acrylates and methacrylates, other copolymerizable monomers which can be copolymerized with the hydroxyalkyl (meth)acrylates include ethylenically unsaturated materials such as monoolefinic and diolefinic hydrocarbons, halogenated monoolefinic and diolefinic hydrocarbons, unsaturated esters of organic and inorganic acids, amides and esters of unsaturated acids, nitriles and unsaturated acids and the like. Examples of such monomers include styrene, 1,3-butadiene, acrylamide, acrylonitrile, α -methyl styrene, α -methyl chlorostyrene, vinyl butyrate,

vinyl acetate, alkyl chloride, divinyl benzene, diallyl itaconate, triallyl cyanurate and mixtures thereof. Preferably, these other ethylenically unsaturated materials are used in admixture with the above-mentioned acrylates and methacrylates.

In certain embodiments of the invention, the polyol may be a polyurethane polyol. These polyols can be prepared by reacting any of the above-mentioned polyols with a minor amount of polyisocyanate (OH/NCO equivalent ratio greater than 1:1) so that free primary hydroxyl groups are present in the product. In addition to the high molecular weight polyols mentioned above, mixtures of both high molecular weight and low molecular weight polyols such as those mentioned above may be used.

Suitable hydroxy-functional polycarbonate polyols may be those prepared by reacting monomeric diols (such as 1,4-butanediol, 1,6-hexanediol, di-, tri- or tetraethylene glycol, di-, tri- or tetrapropylene glycol, 3-methyl-1,5-pentanediol, 4,4'-dimethylolcyclohexane and mixtures thereof) with diaryl carbonates (such as diphenyl carbonate, dialkyl carbonates (such as dimethyl carbonate and diethyl carbonate), alkylene carbonates (such as ethylene carbonate or propylene carbonate), or phosgene. Optionally, a minor amount of higher functional, monomeric polyols, such as trimethylolpropane, glycerol or pentaerythritol, may be used.

In various embodiments, the azidated polyols are the reaction products of a polyol and methane sulfonyl chloride (or toluenesulfonyl (tosyl), p-bromophenylsulfonfyl (brosyl), benzyl) in presence of base, followed by displacement of the methanesulfonate by an azide anion using NaN_3 . Another method to produce azidated polyols is the reaction of a polyoxirane compound, for example, a (meth)acrylic polymer containing glycidyl methacrylate comonomer units, with an azide ion using, for example, NaN_3 . Any polyol, including but not limited to, those disclosed herein may be azidated and useful in the invention.

The azidated polyol useful in the present application may have a nitrogen content derivable from azide relative to the total weight of the molecule in various embodiment of 20 wt.-% or less, in certain embodiments of 18 wt.-% or less, or of 16 wt.-% or less and in selected embodiments of 15 wt.-% or less. Having such a low azide content helps to ensure that the polyols are sufficiently stable against explosive decomposition, such that extensive handling precautions can be avoided. On the other hand, it is preferred that the nitrogen content derivable from azide relative to the total weight of the molecule in the azide polyol in various embodiments is 1 wt.-% or more, in some embodiments, 2 wt.-% or more, in certain embodiments, 5 wt.-% or more and in selected embodiments, 8 wt.-% or more. Such an azide content ensures that the polyols have a sufficiently low viscosity during handling, but also permits the azidated polyol to contain multiple azide groups.

In various embodiments, the alkyne-containing alkylation agent is an alkynol, in certain embodiments, 2-hydroxyethylpropiolate (2-HEP), as such compounds are readily available and relatively inexpensive. The alkynol has the structure below:



in which R^1 is an electron-withdrawing group selected from carbonyl, ester, amide, and urethane and R^2 is a linear or branched alkyl chain having from 1 to 15 carbon atoms.

The alternative polyurethane compositions of the present invention are obtained by reacting an azide compound having two or more azide groups attached thereto and an alkyne compound having two or more alkyne groups

attached thereto in a 1,3-dipolar cycloaddition of the azide and alkyne groups. This can, for example, be achieved by heating the components to temperatures sufficient to affect the cycloaddition such as in various embodiments, at least 100°C ., in certain embodiments, at least 120°C . and in selected embodiments, at least 140°C .

The quantity of catalyst can vary depending on the specific catalyst used. In some embodiments, the catalyst is used in an amount of up to 5 percent by weight, such as 0.001 to 3 percent by weight, or, in some cases, 0.001 to 2 percent by weight, based on the total weight of the treatment composition. In fact, it has been surprisingly observed that the pot-life of certain compositions suitable for use in the processes of the present invention was actually extended by inclusion of certain organic acid blocked amine catalysts in the composition in an amount of 0.01 to 2, such as 0.1 to 1, percent by weight, based on the total weight of the treatment composition, as compared to the same treatment composition in which no such catalyst is included.

In some embodiments of the present application, the azide/alkyne reaction is preferably catalyzed by a Cu^I -based catalyst as this allows a significant reduction of the reaction temperature to about ambient temperature ($\sim 20^\circ\text{C}$.). The Cu^I -based catalyst may, for example, be a copper-containing surface which contains sufficient Cu^I in the surface layer to provide the required catalytic action. If application of the inventive composition to non copper-containing surfaces is intended, it is necessary that the Cu^I -based catalyst come from a copper source which is not attached to the surface of a material to which the alternative polyurethane composition is to be applied.

Suitable copper catalysts of this type can be based on commercially available Cu^I salts such as CuBr or CuI . It has been noted that Cu^I precursors do not provide catalysts with high reactivities in the formation of 1,4-disubstituted triazols when azide compounds having two or more azide groups attached thereto and alkyne compounds having two or more alkyne groups attached to a molecule are reacted; however, Cu^{II} precursors which are converted to Cu^I by the action of a reducing agent, provide enhanced activity. Suitable Cu^{II} precursors include, but are not limited to, copper(II) sulfate, copper(II) acetate monohydrate, and copper(II) 2-ethylhexanoate. Suitable reducing agents include for example triphenyl phosphine, sodium ascorbate, tin(II) 2-ethylhexanoate, and hydroquinone.

In various embodiments, the alternative polyurethane compositions of the present invention may be used to provide coatings, adhesives, sealants, films, elastomers, castings, foams, and composites.

The alternative polyurethane compositions of the present invention may further include any of a variety of additives such as defoamers, devolatilizers, surfactants, thickeners, flow control additives, colorants (including pigments and dyes) or surface additives.

The alternative polyurethane compositions of the invention may be contacted with a substrate by any methods known to those skilled in the art, including but not limited to, spraying, dipping, flow coating, rolling, brushing, pouring, and the like. In some embodiments, the inventive compositions may be applied in the form of paints or lacquers onto any compatible substrate, such as, for example, metals, plastics, ceramics, glass, and natural materials. In certain embodiments, the inventive composition is applied as a single layer. In other embodiments, the composition of the present invention may be applied as multiple layers as needed.

The non-limiting and non-exhaustive examples that follow are intended to further describe various non-limiting and non-exhaustive embodiments without restricting the scope of the embodiments described in this specification. All quantities given in “percents” are understood to be by weight, unless otherwise indicated. For the purpose of mass

to mole conversions, reagents with purity of 99% or higher are considered to be 100% pure.

Although described herein in the context of a coating, those skilled in the art will recognize that the principles of the present invention are equally applicable to adhesives, sealants, films, elastomers, castings, foams, and composites.

The following materials were used in preparation of the Examples:

POLYISOCYANATE A	an allophanate-modified polyisocyanate having isocyanate equivalent weight of 217.72 g/eq, commercially available from Covestro LLC (Pittsburgh, PA) as DESMODUR XP 2580 (19.3% isocyanate);
POLYOL A	an acrylic polyol, received as a 80% solids solution in n-BA, commercially available from Allnex as SETALUX DA 870 BA, possessing hydroxyl equivalent weight of 461.02 g/eq (at 100% solids);
POLY(ALKYNYL CARBAMATE) PREPOLYMER A	a proprietary prepolymer based on POLYISOCYANATE A, having an alkyne equivalent weight 273.78 g/eq (at 100% solids);
POLY(ALKYNYL CARBAMATE) PREPOLYMER B	a proprietary prepolymer based on POLYISOCYANATE A, having an alkyne equivalent weight 331.82 g/eq (at 100% solids);
AZIDATED POLYOL A	a proprietary prepolymer based on POLYOL A, having azide equivalent weight of 532.74 g/eq (at 91.23% solids); the solid % was determined by drying an aliquot in an oven and recording the fractional weight remaining;
4 Å Molecular Sieves	Fisher Scientific, Type 4A, Grade 514, 8-12 Mesh beads, 4 Å pore size, activated using a microwave oven prior to use;
ALKYNOL A	propargyl alcohol (99%), commercially available from Fisher Scientific; reagent was dried over 4 Å molecular sieves prior to use;
ALKYNOL B	2-hydroxyethyl propiolate;
TEA	triethylamine (≥99.5%), commercially available from Sigma-Aldrich; reagent was dried over 4 Å molecular sieves prior to use;
MeCN	acetonitrile (OPTIMA), commercially available from Fisher Scientific; solvent was distilled and dried over 4 Å molecular sieves prior to use;
Mesyl-Cl	methanesulfonyl chloride (≥99.7%), commercially available from Sigma-Aldrich;
PMDETA	N,N,N',N''-pentamethyldiethylenetriamine ligand (99%), commercially available from Sigma-Aldrich;
DCM	dichloromethane (Certified ACS), commercially available from Fisher Scientific;
DMF	N,N-dimethylformamide (Certified ACS), commercially available from Fisher Scientific;
NaN ₃	sodium azide (REAGENTPLUS, ≥99.5%), commercially available from Sigma-Aldrich;
n-BA	n-butyl acetate, ACS reagent, ≥99.5%, commercially available from Sigma-Aldrich; solvent was distilled and dried over 4 Å molecular sieves prior to use;
MEK	methyl ethyl ketone, Certified ACS, commercially available from Sigma-Aldrich;
Ethyl acetate	Certified ACS, commercially available from Fisher Scientific;
CATALYST A	dibutyltin dilaurate (DB TDL 98%), commercially available from Strem Chemicals;
CATALYST B	a proprietary CuCl ₂ [PMDETA] catalyst complex;
Brine	saturated aqueous solution of NaCl, prepared by dissolving 450 g NaCl (certified ACS, Fisher Scientific) into 1.2 L of DI water at room temperature;
Toluene	Certified ACS, commercially available from Fisher Scientific;
Benzene	anhydrous, 99.8%, commercially available from Sigma-Aldrich;
Ethylene glycol	anhydrous, 99.8%, commercially available from Sigma-Aldrich;
Hexanes	Certified ACS, commercially available from Fisher Scientific;
Methanol	Certified ACS, commercially available from Fisher Scientific;
p-toluenesulfonic acid mono-hydrate	ReagentPlus, ≥ 99.8%, commercially available from Sigma-Aldrich;
MgSO ₄	magnesium sulfate, anhydrous, commercially available from Fisher Scientific; and,

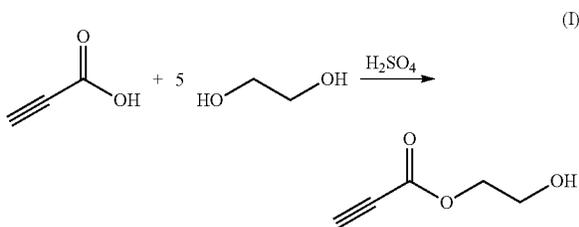
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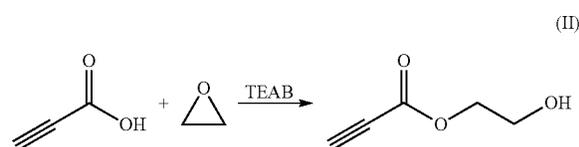
CuCl_2 copper(II) chloride, 97%, commercially available from Sigma-Aldrich.

ALKYNOL B, 2-hydroxyethyl propiolate, used in the synthesis of POLY(ALKYNYL CARBAMATE) PREPOLYMER B can be obtained by several different synthetic routes. Some examples include, but are not limited to, the following:

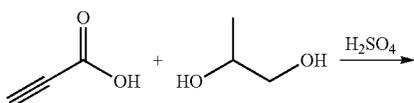
Route I: Preparation of 2-hydroxyethyl propiolate from ethylene glycol; propiolic acid (9.646 g; 137.7 mmol), toluene (300 mL), and ethylene glycol (42.763 g; 688.94 mmol) were charged into a 500 mL round bottom flask. One drop of sulfuric acid was added to the mixture and magnetic stirring was begun. A Dean-Stark apparatus was attached to the flask, and the reaction was heated to reflux and allowed to continue refluxing for 48 hours. The flask was cooled, upon the reaction mixture separated into two layers. The bottom, oily layer was collected, and subjected to flash chromatography (50:50 hexanes/ethyl acetate spiked with 5% methanol as eluent) to yield a yellow oil.



Route II: Preparation of 2-hydroxyethyl propiolate from ethylene oxide; 2-hydroxyethyl propiolate can be prepared using a modification of a procedure reported by Miller et al., in U.S. Pat. No. 3,082,242, which involves reacting propiolic acid with ethylene oxide in the presence of triethyl ammonium bromide.

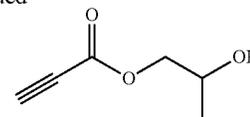


Route III: Preparation of 2-hydroxypropyl propiolate from 1,2-propanediol; a modification of the procedure used to prepare 2-hydroxyethyl propiolate from ethylene glycol can be used to prepare 2-hydroxypropyl propiolate from 1,2-propanediol. The difference in reactivity between primary and secondary alcohols allows reaction of the two reagents at 1:1 stoichiometry and may even reduce the need for flash chromatography for purification purposes.

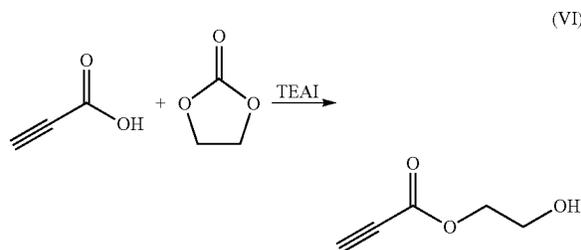


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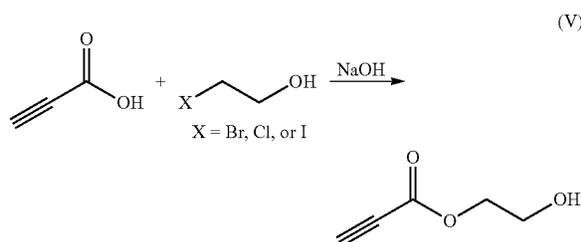
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Route IV: Preparation of 2-hydroxyethyl propiolate from ethylene carbonate; propiolic acid can be reacted with ethylene carbonate as a safer alternative to ethylene oxide. For example, 2-hydroxyethyl propiolate can be prepared from propiolic acid and a slight excess (10 mol %) ethylene carbonate and catalytic amount of triethylammonium iodide using a modification of a procedure reported by Yoshino et al. (Yoshino, T.; Inaba, S.; Komura, H.; Ishido, Y. *J. Chem. Soc. Perkin Trans. 1* 1977, No. 11, 1266-1272). These authors showed that this reaction resulted in high yield of the hydroxy ester when using benzoic acid.

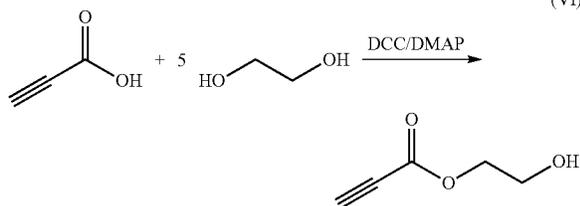


Route V: preparation of 2-hydroxyethyl propiolate from 2-haloethanol; 2-hydroxyethyl propiolate can be prepared from propiolic acid and excess halogenated alcohol such as 2-chloroethanol or 2-bromoethanol in the presence of a base such as sodium hydroxide using a modification of a procedure reported by Tang et al. (Tang, W.; Huang, Y.; Qing, F.-L. *J. Appl. Polym. Sci.* 2011, 119, 84-92). These authors demonstrated a similar reaction using acrylic acid with 2-chloroethanol.

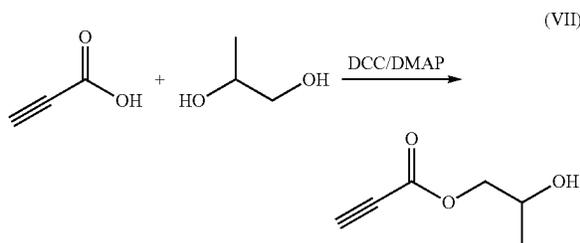


Route VI: Preparation of 2-hydroxyethyl propiolate from ethylene glycol; 2-hydroxyethyl propiolate can be prepared from propiolic acid and ethylene glycol using dicyclohexylcarbodiimide (DCC)/4-(dimethylamino)pyridine (DMAP) coupling at -30°C . using a modification of a procedure reported by Hodgson et al. (Hodgson, D. M.; Talbot, E. P. A.; Clark, B. P. *Org. Lett.* 2011, 13 (21), 5751-5753). These authors showed that a similar unsaturated hydroxy ester could be made in this fashion.

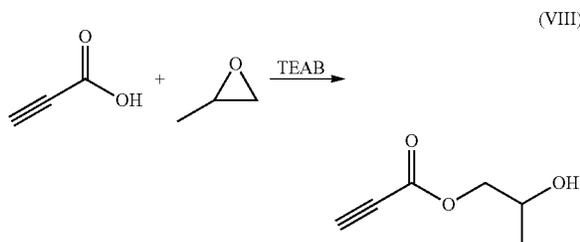
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Route VII: Preparation of 2-hydroxypropylpropiolate from 1,2-propanediol; a modification of the procedure for the preparation of 2-hydroxyethylpropiolate from ethylene glycol using dicyclohexylcarbodiimide (DCC)/4-(dimethylamino)pyridine (DMAP) coupling can be used to prepare 2-hydroxypropyl propiolate from propiolic acid and 1,2-propanediol.



Route VIII: Preparation of 2-hydroxypropylpropiolate from 1,2-propanediol; a modification of the procedure used to prepare of 2-hydroxyethylpropiolate from ethylene oxide can be used to prepare 2-hydroxypropyl propiolate from propiolic acid and propylene oxide.



Synthesis of POLY(ALKYNYL CARBAMATE) PREPOLYMER A

All glassware was cleaned and dried in an oven overnight. The following procedure was performed in a N₂-protected, dry box equipped with a cryostated heptane bath. POLYISOCYANATE A (101.02 g, 0.464 mol isocyanate) and CATALYST A (1.09 g, 1.73 mmol) were charged to a 500 mL three-neck round bottom flask equipped with a mechanical stirrer, a thermocouple, and an addition funnel. The mixture in the flask was stirred and allowed to equilibrate at 0° C. for 10 minutes. After equilibration, ALKYNOL A (26.102 g, 0.466 mol) was charged to the addition funnel and added into the stirring solution at initially 1 drop/sec. The addition speed was adjusted so that temperature of the reaction would not exceed 30° C. After the addition was

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complete, the mixture was allowed to react overnight, and the product of the reaction was characterized by FTIR, ¹³C-NMR and ¹H-NMR.

Synthesis of ALKYNOL B

All glassware was heated in an oven set to 200° C. for two hours and cooled in vacuo. Benzene (400 mL), ethylene glycol (55.580 g, 895 mmol), propiolic acid (12.345 g, 167.42 mmol), and p-toluenesulfonic acid mono-hydrate (0.813 g, 4.274 mmol) were added to a one-liter, round-bottom flask equipped with a magnetic stirrer. A Dean-Stark trap and a condenser were fitted to the flask, and the system was continuously purged with Na. The stirred mixture was heated to reflux and allowed to react for 24 hours at which point no additional water was being collected (3.8 mL, theoretical: 3.17 mL). The mixture was cooled to room temperature and concentrated in vacuo yielding a slightly brown oil. The oil was purified using flash chromatography using hexane (HPLC grade, Fisher Scientific) as eluent. The structure of the purified product was verified by 600 MHz ¹H-NMR and was confirmed to be ALKYNOL B (10.80 g; 56.5% yield).

Synthesis of POLY(ALKYNYL CARBAMATE) PREPOLYMER B

All glassware was cleaned and dried in an oven overnight. The following procedure was performed in a N₂-protected dry box equipped with a cryostated heptane bath. POLYISOCYANATE A (19.098 g, 19.3% isocyanate; 0.088 mol isocyanate) and CATALYST A (0.2 g, 0.317 mmol) were charged to a 250 mL, three-neck round bottom flask equipped with a mechanical stirrer, a thermocouple, and an addition funnel. The mixture was stirred and allowed to equilibrate at 0° C. for 10 minutes. After equilibration, ALKYNOL B (10.00 g, 0.088 mol) was charged to the addition funnel and added into the stirring solution at initially 1 drop/sec. The addition speed was adjusted so that temperature of the reaction did not exceed 30° C. After the addition, the mixture was allowed to react overnight, and the product of the reaction was characterized by ¹³C-NMR and ¹H-NMR.

Synthesis of AZIDATED POLYOL A

All glassware was cleaned and dried in an oven overnight. The following procedure was performed in a N₂-protected dry box equipped with a cryostated heptane bath. POLYOL A (151.2 g, 0.262 mol), TEA (55.0 mL, 0.395 mol) and MeCN (300 mL) were charged to a one-liter, two-neck, round-bottom flask equipped with a mechanical stirrer and an addition funnel. The mixture was stirred and allowed to equilibrate at 0° C. for 10 minutes. After equilibration, a solution of mesyl-Cl, (24.0 mL, 0.310 mol) in MeCN (50 mL) was charged to the addition funnel and added into the stirring solution at 1 drop/sec. After the addition, the mixture was allowed to react overnight.

The reaction flask was transferred out of the dry box, and the mixture was filtered to remove the TEA salts. MeCN and excess TEA were vacuum stripped, and the mesylated resin was re-dissolved into ethyl acetate (500 mL). The solution was washed with 20/80 (v/v) brine/DI water mixture (3×300 mL) and brine (300 mL) and dried with MgSO₄ overnight. Ethyl acetate was removed by vacuum stripping to afford the

mesylated POLYOL A as an intermediate. An aliquot was taken to perform FTIR, ^{13}C -NMR, and ^1H -NMR characterization.

The mesylated resin was then redissolved in MeCN (300 mL) and DMF (30 mL) in a one-liter, one-neck round bottom flask. NaN_3 (20.0 g, 0.308 mol) and a stir bar were added to the mixture, and the flask was equipped with a condenser sealed with a rubber septum with a needle. The mixture was stirred at 95°C . for 16 hours, allowed to cool to room temperature, and filtered to remove the Na mesylate salts. MeCN was vacuum stripped, and the azidated resin was re-dissolved into ethyl acetate (500 mL). The solution was washed with 20/80 (v/v) brine/DI water mixture (3x300 mL) and brine (3x300 mL) and dried with MgSO_4 overnight. The final product, AZIDATED POLYOL A, was isolated by removal of ethyl acetate by vacuum stripping and thereafter characterized by FTIR, ^{13}C -NMR, and ^1H -NMR. An aliquot of the product was placed on an aluminum pan and dried in the oven at 100°C . for one hour.

Synthesis of CATALYST B

CuCl_2 (0.993 g; 7.16 mmol), and MeCN (7.5 mL) were charged to a 100 mL single-neck, round-bottom flask. PMDETA (1.283 g; 7.40 mmol) was added dropwise to the stirred solution. Upon the addition, the reaction turned from a brown color to turquoise. After reacting at room temperature for 24 hours, the MeCN was removed in vacuo to yield the product as a blue powder.

Fourier transform infrared spectroscopy (FTIR) studies were conducted using a NICOLET 8700 spectrometer with a KBr beam splitter and a DTGS detector. Samples were sandwiched between two NaCl salt plates (polished with dichloromethane (DCM) (Certified ACS), approximate thickness: 5 mm). Isothermal real-time Fourier transform infrared spectroscopy (RT-FTIR) was measured using a Thermo Fisher Scientific NICOLET 6700 FTIR equipped with a mid-IR beam splitter and integrated with a Simplex Scientific HT-32 heated transmission cell.

The SIMPLEX software was paired to the OMNIC FTIR software native to the NICOLET 6700. Approximately 1.5 g of sample was charged at 1:1 stoichiometry for NCO:OH, or azide:alkyne, to a scintillation vial and placed in a FLAKTECH mixer and allowed to mix at 1800 rpm for 10-20 minutes until a homogenous mixture was obtained. A small aliquot was taken from the mixture and compressed between two polished NaCl plates. The plates were inserted in the transmission cell and subsequently placed in the chamber for FTIR analysis. The sample chamber was purged with N_2 for approximately 10 minutes to reduce the intensity of the CO_2 peak.

The sample was rapidly heated from room temperature to the desired temperature and spectra were immediately obtained in 1 minute intervals (32 scans; 4 cm^{-1} resolution) for the duration of the run (60 minutes). Conversion was monitored as the diminution of the area of either the isocyanate stretching peak (most typically around 2271 cm^{-1}) or the peak attributed to both azide ($\text{N}=\text{N}=\text{N}$ stretching) and alkyne ($\text{C}\equiv\text{C}$ stretching) at approximately 2100 cm^{-1} . Aliphatic $\text{C}-\text{H}$ stretching (2755 cm^{-1}) was used as an internal standard. Peak areas were determined by integrating above a two-point baseline, of the absorbance centered at 2271 cm^{-1} , associated with the NCO stretching or the absorbance centered at 2100 cm^{-1} , associated with the azide and alkyne stretches.

Proton nuclear magnetic resonance (^1H -NMR) spectra and carbon nuclear magnetic resonance (^{13}C -NMR) spectra were

obtained using a 600.13 MHz Varian Mercury^{plus} NMR (VNMR 6.1C) spectrometer. For ^1H NMR, typical acquisition parameters were 8 s recycle delay, $7.8\text{ }\mu\text{s}$ pulse corresponding to a 45° flip angle, and an acquisition time of 1.998 s. The number of scans acquired for each sample was 64. All ^1H chemical shifts were referenced to tetramethylsilane (TMS) (0 ppm). Sample solutions were prepared at a concentration of approximately 5-10% in deuterated chloroform (CDCl_3) (99.8+ atom % D, 0.03 v/v % TMS) (Acros Organics, further dried using activated molecular sieves prior to use), and the resulting solution was charged to a 5 mm NMR tube.

For ^{13}C NMR, typical acquisition parameters were 1 sec recycle delay, 11 ms pulse corresponding to a 45° flip angle, and an acquisition time of 0.908 s. The number of scans acquired for each sample was 1024. All ^{13}C chemical shifts were referenced to residual chloroform (77.16 ppm). Sample solutions were prepared at a concentration of approximately 30% in CDCl_3 , and the resulting solution was charged to a 5 mm NMR tube.

Differential scanning calorimetry (DSC) was performed using a TA Instruments Q200. For this purpose, coatings were prepared on polyethylene (PE) film substrate. The coatings, which had little adhesion to the PE film, were easily peeled off and punched to give circular samples ($d=0.25\text{ in. (6.35 mm)}$) of the coating films. Stacks of five such samples (total $\sim 5\text{ mg}$) per coating were placed in a hermetically sealed T_{zero} pan. A heat/cool/heat cycle was performed on each stack starting at -50°C . and ending at 200°C . at a rate of 10°C./min . T_g of the cured material was determined from the second heating cycle, and TA Universal Analysis software was used to determine the midpoint of the T_g inflection as the reported value.

Coatings Preparation

FORMULATION A was prepared as follows. POLYOL A (3.105 g) and POLYISOCYANATE A (1.174 g) were added to a scintillation vial. The mixture was placed in a FLAKTECH mixer and mixed at 1800 rpm for 20-30 minutes until a homogenous mixture was obtained. Meanwhile, smooth-finish steel panels (Type QD, Q-Lab Corporation) and polyethylene (PE) films were treated with acetone rinsing to remove surface contaminants. FORMULATION A was then drawn down onto the prepared panels and PE films using a 6 mil wet drawdown bar. The coatings were placed in a VWR Shel lab HF2 oven and subjected to the following pre-programmed curing profile: the solvent was allowed to flash at 30°C . for two hours, and then the temperature was ramped up to 100°C . at 1°C./min . The coatings were cured at 100°C . for four hours and cooled to 30°C .

FORMULATION B was prepared as follows. AZIDATED POLYOL A (3.079 g) and POLY(ALKYNYL CARBAMATE) PREPOLYMER A (1.582 g) were added to a scintillation vial. The mixture was diluted with 0.44 g n-BA, placed in a FLAKTECH mixer, and mixed at 1800 rpm for 20-30 minutes until a homogenous mixture was obtained. Meanwhile, smooth-finish steel panels (Type QD, Q-Lab Corporation) and polyethylene (PE) films were treated with acetone rinsing to remove surface contaminants. FORMULATION B was then drawn down onto the prepared panels and PE films using a 6 mil wet drawdown bar. The coatings were placed in a VWR Shel lab HF2 oven and subjected to the following pre-programmed curing profile: the solvent was allowed to flash at 30°C . for two hours, and the

temperature was ramped up to 100° C. at 1° C./min. The coatings were cured at 100° C. for four hours and cooled to 30° C.

FORMULATION C was prepared as follows AZIDATED POLYOL A (3.081 g) and POLY(ALKYNYL CARBAMATE) PREPOLYMER B (1.919 g) were added to a scintillation vial. The mixture was diluted with 0.44 g n-BA, placed in a FLAKTECH mixer, and mixed at 1800 rpm for 20-30 minutes until a homogenous mixture was obtained. Meanwhile, smooth-finish steel panels (Type QD, Q-Lab Corporation) and polyethylene (PE) films were treated with acetone rinsing to remove surface contaminants. FORMULATION C was then drawn down onto the prepared panels and PE films using a 6 mil wet drawdown bar. The coatings were placed in a VWR Shel lab HF2 oven and subjected to the following pre-programmed curing profile: the solvent was allowed to flash at 30° C. for two hours, and the temperature was ramped up to 100° C. at 1° C./min. The coatings were cured at 100° C. for four hours and cooled to 30° C.

Each coatings formulation was applied onto three smooth-finish steel panels (Type QD, Q-Lab Corporation). Each coating test was conducted in triplicate (one replicate per panel). Coating tests were performed 12 hours after the complete curing profile.

MEK double rubs. Reaction conversion/crosslink density was qualitatively compared via an MEK double rubs test up to 200 rubs using a 32 oz. (0.907 kg) hammer covered by four folds of cheesecloth according to ASTM D5402-15.

Hardness was measured via a pencil hardness test in accordance with ASTM D3363-05.

As can be appreciated by reference to Table I, FORMULATION A was a polyurethane control coating. The same ingredients used in FORMULATION A were modified for azido-alkyne click chemistry and used to create FORMULATIONS B and C. FORMULATION B had POLY(ALKYNYL CARBAMATE) PREPOLYMER A as the alkyne component; whereas FORMULATION C had POLY(ALKYNYL CARBAMATE) prepolymer B as the alkyne component. The difference between POLY(ALKYNYL CARBAMATE) prepolymer A and POLY(ALKYNYL CARBAMATE) prepolymer B was the type of alkyne molecule that was used to obtain the alkyne functionality. POLY(ALKYNYL CARBAMATE) prepolymer A was based on ALKYNOL A and POLY(ALKYNYL CARBAMATE) prepolymer B was based on ALKYNOL B.

TABLE I

FORMULATION	A	B	C
POLYISOCYANATE A	1.174	—	—
POLYOL A	3.105	—	—
POLY(ALKYNYL CARBAMATE) PREPOLYMER A	—	1.582	—
POLY(ALKYNYL CARBAMATE) PREPOLYMER B	—	—	1.919
AZIDATED POLYOL A	—	3.079	3.081

As can be seen by the coating results in Table II, the coating performances of all three FORMULATIONS were very similar to each other. Therefore, properties similar to those of a polyurethane were obtained in azido-alkyne formulations without the use of the traditional isocyanate and polyol route. The azido-alkyne formulations allow the creation of crosslinked polyurethanes that do not involve reaction of isocyanate groups in the final curing step. Use of POLY(ALKYNYL CARBAMATE) prepolymer B, prepared

from ALKYNOL B (i.e., 2-hydroxyethyl propiolate), which possesses a relatively electrophilic alkyne moiety, enables a fully cured coating to be obtained in the absence of an externally-added catalyst.

TABLE II

COATING PERFORMANCE	A	B	C
Pencil Hardness	6H	8H	6H
MEK Double Rubs	>200	>200	>200
T _g (° C.)	46.95	34.87	41.73

Real time cure kinetics studies were performed as follows. To a 20 mL scintillation vial, 5.0235 g AZIDATED POLYOL A, 0.02009 g CATALYST B, and 5 mL of DCM were charged. The three ingredients were mixed until completely homogeneous, and then DCM was removed in vacuo; the complete removal of DCM was verified by ¹H NMR. The resulting 0.40% pre-catalyzed AZIDATED POLYOL A was used as a stock resin for copper catalyzed kinetic studies. All resin pairs were mixed and cured in the same manner. Four different formulations were studied, for a total of 16 different runs. As an example, the AZIDATED POLYOL A and POLY(ALKYNYL CARBAMATE) PREPOLYMER A with 0.40% CATALYST B formulation will be described. To a 20 mL scintillation vial, 0.959 g pre-catalyzed AZIDATED POLYOL A (1.793 mmol) and 0.491 g POLY(ALKYNYL CARBAMATE) PREPOLYMER A (1.793 mmol) were charged and thoroughly mixed.

Immediately prior to FTIR analysis, two drops of tin(II) 2-ethylhexanoate (95%, Sigma-Aldrich) were added to the vial and thoroughly mixed. Results of isothermal runs carried out for 60 minutes at room temperature, 60° C., 80° C., and 100° C., are shown in FIG. 1, FIG. 2, FIG. 3, and FIG. 4, respectively. Conversion was monitored as the diminution of the area of the peak at approximately 2100 cm⁻¹ indicative of both azide and alkyne functionalities.

As can be appreciated by reference to FIG. 1, FIG. 2, FIG. 3, and FIG. 4, four different formulations were tested at four different curing conditions. The formulations were: AZIDATED POLYOL A and POLY(ALKYNYL CARBAMATE) PREPOLYMER A with no CATALYST (open circle, ○), AZIDATED POLYOL A and POLY(ALKYNYL CARBAMATE) PREPOLYMER B with no CATALYST (open downward triangle, ▽), AZIDATED POLYOL A and POLY(ALKYNYL CARBAMATE) PREPOLYMER A with 0.40% CATALYST B (closed circle, ●), and AZIDATED POLYOL A and POLY(ALKYNYL CARBAMATE) PREPOLYMER B with 0.40% CATALYST B (closed downward triangle, ▼). The difference between POLY(ALKYNYL CARBAMATE) PREPOLYMER A and POLY(ALKYNYL CARBAMATE) PREPOLYMER B was the type of alkyne molecule that was used to obtain the alkyne functionality; POLY(ALKYNYL CARBAMATE) PREPOLYMER A was based on ALKYNOL A and POLY(ALKYNYL CARBAMATE) PREPOLYMER B was based on ALKYNOL B. As can be appreciated, at every curing temperature, with or without catalyst, formulations made from POLY(ALKYNYL CARBAMATE) PREPOLYMER B had higher curing kinetics than formulations made from POLY(ALKYNYL CARBAMATE) PREPOLYMER A. In other words, obtaining the alkyne functionality through ALKYNOL B resulted in much faster curing speed than obtaining alkyne functionality through ALKYNOL A.

This specification has been written with reference to various non-limiting and non-exhaustive embodiments.

However, it will be recognized by persons having ordinary skill in the art that various substitutions, modifications, or combinations of any of the disclosed embodiments (or portions thereof) may be made within the scope of this specification. Thus, it is contemplated and understood that this specification supports additional embodiments not expressly set forth herein. Such embodiments may be obtained, for example, by combining, modifying, or reorganizing any of the disclosed steps, components, elements, features, aspects, characteristics, limitations, and the like, of the various non-limiting embodiments described in this specification. In this manner, Applicant reserves the right to amend the claims during prosecution to add features as variously described in this specification, and such amendments comply with the requirements of 35 U.S.C. § 112(a), and 35 U.S.C. § 132(a).

Various aspects of the subject matter described herein are set out in the following numbered clauses:

Clause 1. An alternative polyurethane composition comprising: a reaction product of an azidated polyol and a poly(alkynyl carbamate) prepolymer reacted at a temperature of from 20° C. to 120° C., wherein the poly(alkynyl carbamate) prepolymer comprises a reaction product of a polyisocyanate and a stoichiometric equivalent of an alkynol of the formula (I), $\text{HC}\equiv\text{C}-\text{R}^1\text{R}^2-\text{OH}$ (I), and wherein R^1 is an electron-withdrawing group selected from the group consisting of carbonyl, ester, amide, and urethane and R^2 is a linear or branched alkyl chain having from 1 to 15 carbon atoms.

Clause 2. The alternative polyurethane composition according to Clause 1, wherein the alkynol is 2-hydroxyethyl propiolate.

Clause 3. The alternative polyurethane composition according to one of Clauses 1 and 2, wherein the polyisocyanate is selected from the group consisting of 1,4-tetramethylene diisocyanate, 1,6-hexamethylene diisocyanate, 2,2,4-trimethyl-1,6-hexamethylene diisocyanate, 1,12-dodecamethylene diisocyanate, cyclohexane-1,3-diisocyanate, cyclohexane-1,4-diisocyanate, 1-isocyanato-2-isocyanato-methyl cyclopentane, 1-isocyanato-3-isocyanatomethyl-3,5,5-trimethyl cyclohexane (isophorone diisocyanate or IPDI), bis-(4-isocyanatocyclohexyl)methane, 1,3-bis(isocyanatomethyl)-cyclohexane, 1,4-bis(isocyanatomethyl)-cyclohexane, bis-(4-isocyanato-3-methyl-cyclohexyl)-methane, $\alpha,\alpha,\alpha',\alpha'$ -tetramethyl-1,3-xylene diisocyanate, $\alpha,\alpha,\alpha',\alpha'$ -tetramethyl-1,4-xylene diisocyanate, 1-isocyanato-1-methyl-4(3)-isocyanato-methyl cyclohexane, 2,4-hexahydrotoluene diisocyanate, 2,6-hexahydrotoluene diisocyanate, toluene diisocyanate (TDI), diphenylmethane diisocyanate (MDI), pentane diisocyanate (PDI)—bio-based), and, isomers of any of these; or mixtures of any of these.

Clause 4. The alternative polyurethane composition according to any one of Clauses 1 to 3, wherein the polyisocyanate contains one or more selected from the group consisting of isocyanurate, biuret, allophanate, uretdione, and iminooxadiazine dione groups.

Clause 5. The alternative polyurethane composition according to any one of Clauses 1 to 4, wherein the azidated polyol is a reaction product of a polyol and an azide.

Clause 6. The alternative polyurethane composition according to any one of Clauses 1 to 5, wherein the azidated polyol is a reaction product of a polyol and methane sulfonyl chloride in presence of base, followed by displacement of methanesulfonate by an azide anion.

Clause 7. The alternative polyurethane composition according to one of Clauses 5 and 6, wherein the polyol is

selected from the group consisting of polyalkylene ether polyols, polyester polyols, hydroxyl containing polycaprolactones, hydroxyl-containing (meth)acrylic polymers, polycarbonate polyols, polyurethane polyols and combinations thereof.

Clause 8. The alternative polyurethane composition according to any one of Clauses 1 to 7, wherein the azidated polyol and the poly(alkynyl carbamate) prepolymer are reacted in the presence of a Cu^I -containing catalyst.

Clause 9. The alternative polyurethane composition according to Clause 8, wherein the Cu^I -containing catalyst comprises a Cu^{II} catalyst and a reducing agent.

Clause 10. The alternative polyurethane composition according to one of Clauses 8 and 9, wherein the Cu^{II} catalyst is selected from the group consisting of copper(II) chloride, $\text{CuCl}_2[\text{PMDETA}]$, copper(II) bromide, copper(II) iodide, copper(II) sulfate, copper(II) 2-ethylhexanoate, and copper(II) acetate monohydrate.

Clause 11. The alternative polyurethane composition according to Clause 9, wherein the reducing agent is selected from the group consisting of triphenyl phosphine, sodium ascorbate, tin(II) 2-ethylhexanoate, and hydroquinone.

Clause 12. One of a coating, an adhesive, a sealant, a film, an elastomer, a casting, a foam, and a composite comprising the alternative polyurethane composition according to any one of Clauses 1 to 11.

Clause 13. A substrate having applied thereto the one of a coating, an adhesive, a sealant, a film, an elastomer, a casting, a foam, and a composite according to Clause 12.

Clause 14. A process of producing an alternative polyurethane composition, the process comprising: reacting a polyisocyanate with a stoichiometric equivalent of an alkynol of the formula (I), $\text{HC}\equiv\text{C}-\text{R}^1\text{R}^2-\text{OH}$ (I) to produce a poly(alkynyl carbamate) prepolymer, and reacting the poly(alkynyl carbamate) prepolymer with an azidated polyol at a temperature of from 20° C. to 120° C. to produce the alternative polyurethane composition, wherein IV is an electron-withdrawing group selected from the group consisting of carbonyl, ester, amide, and urethane and R^2 is a linear or branched alkyl chain having from 1 to 15 carbon atoms.

Clause 15. The process according to Clause 14, wherein the alkynol is 2-hydroxyethyl propiolate.

Clause 16. The process according to one of Clauses 14 and 15, wherein the polyisocyanate is selected from the group consisting of 1,4-tetramethylene diisocyanate, 1,6-hexamethylene diisocyanate, 2,2,4-trimethyl-1,6-hexamethylene diisocyanate, 1,12-dodecamethylene diisocyanate, cyclohexane-1,3-diisocyanate, cyclohexane-1,4-diisocyanate, 1-isocyanato-2-isocyanato-methyl cyclopentane, 1-isocyanato-3-isocyanatomethyl-3,5,5-trimethyl cyclohexane (isophorone diisocyanate or IPDI), bis-(4-isocyanatocyclohexyl)methane, 1,3-bis(isocyanatomethyl)-cyclohexane, 1,4-bis(isocyanatomethyl)-cyclohexane, bis-(4-isocyanato-3-methyl-cyclohexyl)-methane, $\alpha,\alpha,\alpha',\alpha'$ -tetramethyl-1,3-xylene diisocyanate, $\alpha,\alpha,\alpha',\alpha'$ -tetramethyl-1,4-xylene diisocyanate, 1-isocyanato-1-methyl-4(3)-isocyanato-methyl cyclohexane, 2,4-hexahydrotoluene diisocyanate, 2,6-hexahydrotoluene diisocyanate, toluene diisocyanate (TDI), diphenylmethane diisocyanate (MDI), pentane diisocyanate (PDI)—bio-based), and, isomers of any of these; or mixtures of any of these.

Clause 17. The process according to any one of Clauses 14 to 16, wherein the polyisocyanate contains one or more selected from the group consisting of isocyanurate, biuret, allophanate, uretdione, and iminooxadiazine dione groups.

Clause 18. The process according to any one of Clauses 14 to 17, wherein the azidated polyol is a reaction product of a polyol and an azide.

Clause 19. The process according to any one of Clauses 14 to 18, wherein the azidated polyol is a reaction product of a polyol and methane sulfonyl chloride in presence of base, followed by displacement of methanesulfonate by an azide anion.

Clause 20. The process according to one of Clauses 18 and 19, wherein the polyol is selected from the group consisting of polyalkylene ether polyols, polyester polyols, hydroxyl containing polycaprolactones, hydroxyl-containing (meth)acrylic polymers, polycarbonate polyols, polyurethane polyols and combinations thereof.

Clause 21. The process according to any one of Clauses 14 to 20, wherein the azidated polyol and the poly(alkynyl carbamate) prepolymer are reacted in the presence of a Cu^I -containing catalyst.

Clause 22. The process according to Clause 21, wherein the Cu^I -containing catalyst comprises a Cu^{II} catalyst and a reducing agent.

Clause 23. The process according to one of Clauses 21 and 22, wherein the CO catalyst is selected from the group consisting of copper(II) chloride, CuCl_2 [PMDETA], copper(II) bromide, copper(II) iodide, copper(II) sulfate, copper(II) 2-ethylhexanoate, and copper(II) acetate monohydrate.

Clause 24. The process according to Clause 22, wherein the reducing agent is selected from the group consisting of triphenyl phosphine, sodium ascorbate, tin(II) 2-ethylhexanoate, and hydroquinone.

Clause 25. One of a coating, an adhesive, a sealant, a film, an elastomer, a casting, a foam, and a composite comprising the alternative polyurethane composition made according to the process of any one of Clauses 14 to 24.

Clause 26. A substrate having applied thereto the one of a coating, an adhesive, a sealant, a film, an elastomer, a casting, a foam, and a composite according to Clause 25.

What is claimed is:

1. An alternative polyurethane composition comprising: a reaction product of an azidated polyol and a poly(alkynyl carbamate) prepolymer reacted at a temperature of from 20° C. to 120° C.,

wherein the poly(alkynyl carbamate) prepolymer comprises a reaction product of a polyisocyanate and a stoichiometric equivalent of an alkynol of the formula (I),



and

wherein R^1 is an electron-withdrawing group selected from the group consisting of carbonyl, ester, amide, and urethane and R^2 is a linear or branched alkyl chain having from 1 to 15 carbon atoms.

2. The alternative polyurethane composition according to claim 1, wherein the alkynol is 2-hydroxyethyl propiolate.

3. The alternative polyurethane composition according to claim 1, wherein the polyisocyanate is selected from the group consisting of 1,4-tetramethylene diisocyanate, 1,6-hexamethylene diisocyanate, 2,2,4-trimethyl-1,6-hexamethylene diisocyanate, 1,12-dodecamethylene diisocyanate, cyclohexane-1,3-diisocyanate, cyclohexane-1,4-diisocyanate, 1-isocyanato-2-isocyanato-methyl cyclopentane, 1-isocyanato-3-isocyanatomethyl-3,5,5-trimethyl cyclohexane (isophorone diisocyanate or IPDI), bis-(4-isocyanatocyclohexyl)methane, 1,3-bis(isocyanatomethyl)-cyclohexane, 1,4-bis(isocyanatomethyl)-cyclohexane, bis-(4-isocyanato-3-methyl-cyclohexyl)-methane, $\alpha,\alpha,\alpha',\alpha'$ -

tetramethyl-1,3-xylene diisocyanate, $\alpha,\alpha,\alpha',\alpha'$ -tetramethyl-1,4-xylene diisocyanate, 1-isocyanato-1-methyl-4(3)-isocyanato-methyl cyclohexane, 2,4-hexahydrotoluene diisocyanate, 2,6-hexahydrotoluene diisocyanate, toluene diisocyanate (TDI), diphenylmethane diisocyanate (MDI), pentane diisocyanate (PDI)—bio-based), and, isomers of any of these; or mixtures of any of these.

4. The alternative polyurethane composition according to claim 1, wherein the polyisocyanate contains one or more selected from the group consisting of isocyanurate, biuret, allophanate, uretdione, and iminooxadiazine dione groups.

5. The alternative polyurethane composition according to claim 1, wherein the azidated polyol is a reaction product of a polyol and an azide.

6. The alternative polyurethane composition according to claim 5, wherein the polyol is selected from the group consisting of polyalkylene ether polyols, polyester polyols, hydroxyl containing polycaprolactones, hydroxyl-containing (meth)acrylic polymers, polycarbonate polyols, polyurethane polyols and combinations thereof.

7. The alternative polyurethane composition according to claim 1, wherein the azidated polyol and the poly(alkynyl carbamate) prepolymer are reacted in the presence of a Cu^I -containing catalyst.

8. The alternative polyurethane composition according to claim 7, wherein the Cu^I containing catalyst comprises a Cu^{II} catalyst and a reducing agent.

9. The alternative polyurethane composition according to claim 8, wherein the Cu^{II} catalyst is selected from the group consisting of copper(II) chloride, CuCl_2 [PMDETA], copper(II) bromide, copper(II) iodide, copper(II) sulfate, copper(II) 2-ethylhexanoate, and copper(II) acetate monohydrate.

10. The alternative polyurethane composition according to claim 8, wherein the reducing agent is selected from the group consisting of triphenyl phosphine, sodium ascorbate, tin(II) 2-ethylhexanoate, and hydroquinone.

11. One of a coating, an adhesive, a sealant, a film, an elastomer, a casting, a foam, and a composite comprising the alternative polyurethane composition according claim 1.

12. A substrate having applied thereto the one of a coating, an adhesive, a sealant, a film, an elastomer, a casting, a foam, and a composite according to claim 11.

13. A process of producing an alternative polyurethane composition, the process comprising: reacting a polyisocyanate with a stoichiometric equivalent of an alkynol of the formula (I),



to produce a poly(alkynyl carbamate) prepolymer, and reacting the poly(alkynyl carbamate) prepolymer with an azidated polyol at a temperature of from 20° C. to 120° C. to produce the alternative polyurethane composition, wherein R^1 is an electron-withdrawing group selected from the group consisting of carbonyl, ester, amide, and urethane and R^2 is a linear or branched alkyl chain having from 1 to 15 carbon atoms.

14. The process according to claim 13, wherein the alkynol is 2-hydroxyethyl propiolate.

15. The process according to claim 13, wherein the polyisocyanate is selected from the group consisting of 1,4-tetramethylene diisocyanate, 1,6-hexamethylene diisocyanate, 2,2,4-trimethyl-1,6-hexamethylene diisocyanate, 1,12-dodecamethylene diisocyanate, cyclohexane-1,3-diisocyanate, cyclohexane-1,4-diisocyanate, 1-isocyanato-2-isocyanato-methyl cyclopentane, 1-isocyanato-3-isocyanatomethyl-3,5,5-trimethyl cyclohexane (isophorone diisocyanate or IPDI), bis-(4-isocyanatocyclohexyl)methane, 1,3-bis(iso-

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cyanatomethyl)-cyclohexane, 1,4-bis(isocyanatomethyl)-cyclohexane, bis-(4-isocyanato-3-methyl-cyclohexyl)-methane, $\alpha,\alpha,\alpha',\alpha'$ -tetramethyl-1,3-xylene diisocyanate, $\alpha,\alpha,\alpha',\alpha'$ -tetramethyl-1,4-xylene diisocyanate, 1-isocyanato-1-methyl-4(3)-isocyanato-methyl cyclohexane, 2,4-hexahydro-5 toluene diisocyanate, 2,6-hexahydro-10 toluene diisocyanate (TDI), diphenylmethane diisocyanate (MDI), pentane diisocyanate (PDI)—bio-based), and, isomers of any of these; or mixtures of any of these.

16. The process according to claim 13, wherein the polyisocyanate contains one or more selected from the group consisting of isocyanurate, biuret, allophanate, uretdione, and iminooxadiazine dione groups.

17. The process according to claim 13, wherein the azidated polyol is a reaction product of a polyol and an azide.

18. The process according to claim 17, wherein the polyol is selected from the group consisting of polyalkylene ether polyols, polyester polyols, hydroxyl containing polycaprolactones, hydroxyl-containing (meth)acrylic polymers, polycarbonate polyols, polyurethane polyols and combinations thereof.

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19. The process according to claim 13, wherein the step of reacting the azidated polyol and the poly(alkynyl carbamate) prepolymer occurs in the presence of a Cu^I -containing catalyst.

20. The process according to claim 19, wherein the Cu^I -containing catalyst comprises a Cu^{II} catalyst and a reducing agent.

21. The process according to claim 20, wherein the Cu^I catalyst is selected from the group consisting of copper(II) chloride, $\text{CuCl}_2[\text{PMDETA}]$, copper(II) bromide, copper(II) iodide, copper(II) sulfate, copper(II) 2-ethylhexanoate, and copper(II) acetate monohydrate.

22. The process according to claim 20, wherein the reducing agent is selected from the group consisting of triphenyl phosphine, sodium ascorbate, tin(II) 2-ethylhexanoate, and hydroquinone.

23. One of a coating, an adhesive, a sealant, a film, an elastomer, a casting, a foam, and a composite comprising the alternative polyurethane composition made according to the process of claim 13.

24. A substrate having applied thereto the one of a coating, an adhesive, a sealant, a film, an elastomer, a casting, a foam, and a composite according to claim 23.

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